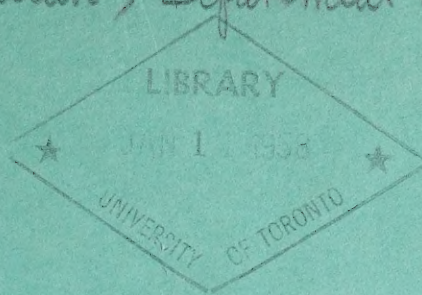


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**CHEMICAL METHODS FOR
ANALYSIS OF FRUIT AND VEGETABLE PRODUCTS**

Assembled and Edited

by

J. A. RUCK

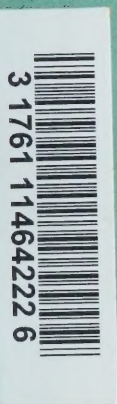
CONTRIBUTION No. 350

CHEMISTRY DIVISION — SCIENCE SERVICE

CANADA DEPARTMENT OF AGRICULTURE

SUMMERLAND, B.C.

DECEMBER, 1956



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PREFACE TO THE SERIES

The application of chemistry to the solution of problems in animal, plant and soil science entails the development and standardization of methods applicable to the material under study. Chemical methods of soil analysis were compiled in 1946 and revised 1949. Chemical methods of plant analysis were assembled in 1953. This compilation of chemical methods for analysis of fruit and vegetable products has been undertaken by Mr. Ruck to meet the demands of another group of analysts. These booklets are for the convenience of laboratory personnel: they do not take the place of standard works such as the A.O.A.C. Methods of Analysis.

A. R. G. Emslie, Chief,
Chemistry Division,
December, 1956.

RESULTS OF THE STUDY

The investigation of the study was conducted in
accordance with the following objectives:
1. To determine the effect of the study on the
performance of the subjects.
2. To determine the effect of the study on the
mood of the subjects.
3. To determine the effect of the study on the
physiological response of the subjects.
4. To determine the effect of the study on the
behavior of the subjects.
5. To determine the effect of the study on the
cognitive function of the subjects.
6. To determine the effect of the study on the
emotional state of the subjects.
7. To determine the effect of the study on the
social interaction of the subjects.
8. To determine the effect of the study on the
overall well-being of the subjects.

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FOREWORD

The methods for analysis of fruit and vegetable processed products that have been assembled and edited in this publication by Mr. Ruck are ones that have been used and checked by various individuals in the Fruit and Vegetable Processing Laboratory at Summerland, B. C. This Laboratory, in addition to developing new products and improving established ones, also performs the necessary chemical analyses for inspectors of Marketing Service. It is hoped that this compilation will prove of value to other investigators and control chemists.

F. E. Atkinson, Head

Fruit & Vegetable Processing Laboratory.

December 31, 1956.

SUMMERLAND FRUIT & VEGETABLE PROCESSING LABORATORY STAFF

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CHEMICAL METHODS FOR ANALYSIS OF FRUIT AND VEGETABLE PRODUCTS

INTRODUCTION

The Analytical Chemistry Unit of the Chemistry Division is responsible for analyses of a wide variety of fruit and vegetable products. Inorganic and organic constituents are determined. The scope of work includes the analysis of commercial fruit product samples, research with new products, and the development of procedures for use in establishing grades and standards. In addition, special problems in the fruit and vegetable processing industry are investigated.

Analytical methods are constantly changing through revision and the adoption of new techniques. Such procedures must be thoroughly checked and repeated before they can be recommended for general use in research and control work. The methods selected for inclusion in this publication are those most commonly carried out on the products listed and are in current use at the Summerland Fruit and Vegetable Products Laboratory. In some cases the procedures have been modified to apply to specific products and have proved to be reliable and accurate. Some of the methods have been in use for many years; others have been adopted only recently. These methods should prove useful for all units and laboratories engaged in fruit and vegetable research, and particularly for new personnel.

Following the outline of each procedure a list of references is given which constitutes acknowledgment of information used in this publication.

CHEMICALS

Unless otherwise noted, all reagents mentioned in the following procedures are of C.P. grade or equivalent quality. Reagents commonly used, such as the mineral acids, ammonia, etc., are not included in the lists of reagents for individual procedures. When they are mentioned in procedures, it is understood that C.P. concentrated reagents are intended. Concentrations of reagent solutions are indicated as percentage values on a weight/volume basis, that is, a definite weight of solid reagent is dissolved in water and made up to a total volume of 100 ml. Concentrations of liquid reagents are similarly indicated as percentage values. This means that the given volume of the concentrated reagent is to be diluted to a total volume of 100 ml. with water unless otherwise stated. Where water is mentioned in any procedure, it is understood to be distilled water.

Technical grade chemicals usually cost appreciably less than C.P. chemicals and, where permissible, they should be used. For example, in a desiccator, technical calcium chloride is used; for a sodium carbonate trap, technical grade is suitable; in preparing cleaning solution, technical sulfuric acid is satisfactory.

APPARATUS AND EQUIPMENT

Special apparatus and equipment required for the various procedures will be found in the description of the analytical method involved. Unless otherwise stated, temperatures mentioned are understood to be in degrees centigrade.

CALCULATION OF RESULTS

The results of analyses of food products are usually expressed in terms of the fresh weight or on a moisture-free basis. The values in the following procedures are expressed in terms of percentage by weight or percentage by volume of the original product. When the constituent is present in small amounts, it is usually expressed as parts per million (p.p.m.), milligrams per kilogram, milligrams per liter, or, as in the case of ascorbic acid, as milligrams per 100 gm. or 100 ml.

The weights and aliquots suggested in the procedures are usually sufficient where an average amount of the constituent is present. In some cases a more suitable weight or aliquot of the sample may have to be determined by experiment.

JAMS, JELLIES AND MARMALADES

WATER-INSOLUBLE SOLIDS

METHOD NO. 1

Principle

A weighed sample is filtered through previously dried and weighed filter paper, washed with hot water and the insoluble solids dried in an oven and weighed.

Preparation of sample

Remove $1/3$ to $1/2$ of the sample from the container and blend for 1 to 2 minutes in a Waring blender. The sample should be taken vertically through the container to avoid removing excess berries or seeds which may have floated to the top. If there are less than 2 lb. in the container, blend entire contents.

Procedure

Weigh to the nearest 0.01 gm. duplicate 25 gm. samples of the blended material. Transfer each duplicate with hot water to a 400 ml. beaker, make to about 200 ml. mark with water, mix and boil gently for 15 to 20 minutes. At intervals replace water lost by evaporation. Transfer one of the duplicate samples to a 250 ml. volumetric flask, cool and make up to volume at 20°. (The filtrate from this is used later for acidity determination.) Filter separately the sample from the volumetric flask and from the beaker through No. 4 Whatman paper which has been previously dried in an oven overnight and weighed in a covered weighing dish. Wash with 800 ml. of hot water, loosening the water-insoluble solids from filter paper with each addition. Transfer filter paper to original weighing dish. Dry overnight at 100 to 110°, cool in desiccator and weigh.

Calculations

% water-insoluble solids = wt. of dry insoluble material x 4.

Jams, Jellies and Marmalades

METHOD NO. 2

Rapid Method Using Moisture Teller Model 271T ¹.

This procedure is particularly useful where the number of determinations is small and where results of analyses are required in a very short time, as in plant control operations.

Procedure

Fit 15 cm. circle of No. 4 Whatman filter paper into 12.5 cm. Buchner funnel, turning up the edges, add half of 7 cm. circle of filter paper to be used to wipe insoluble solids from Buchner funnel after filtration and washing sample, wash with 100 to 200 ml. boiling water, apply suction and dry, using Moisture Teller pan or forced draft oven. Transfer to weighing dish, cool, and weigh. (Approximate time of drying, 5 minutes at $102^{\circ} \pm 3^{\circ}$.)

Weigh 25 or 50 gm. of blended sample to nearest 0.01 gm., transfer with hot water to 400 ml. beaker, adjust to about 200 ml. with water, stir, and boil for 15 to 20 minutes. Place prepared filter in Buchner funnel, attach the funnel to suction flask, but do not connect flask to suction line. Pour 50 to 100 ml. of boiling water on filter and, when a steady flow of water passes through filter, transfer in portions the sample to the filter. Wash insoluble solids with 800 ml. of hot water. In washing, keep solids from forming a tight mat on the surface by adding water in portions. Apply suction after concluding the washing and aspirate to remove last remaining drops of water. Transfer paper and water-insoluble solids to Moisture Teller pan, using extra piece of weighed filter paper to complete transfer, and dry at $102^{\circ} \pm 3^{\circ}$ for 15 minutes. After drying, transfer sample to weighing dish, cool in desiccator and weigh.

¹H. W. Dietert Co., 9330 Roselawn Ave., Detroit 4, Michigan, U.S.A.

Calculations

See Method No. 1

Jams, Jellies and Marmalades

TOTAL ACIDITY

Principle

Total acidity is determined by titrating an aliquot of the water extract with standard sodium hydroxide to pH 8.1 using a pH meter.

Procedure

Use the filtrate from the previous water-insoluble solids determination as in Method I or II. Pipette 50 ml. of the filtrate into 250 ml. beaker. Add about 100 ml. water and titrate with 0.1N NaOH to pH 8.1 using a pH meter. Record the amount of NaOH required and calculate total acidity.

Note: If sugar analysis is required on the sample, record amount of NaOH required to give pH 7.

Calculations

Total acidity is expressed as the percentage of the predominant acid in the fruit. In the case of small fruits such as strawberries, raspberries, black currants, gooseberries and citrus fruits, this is expressed as citric acid. The acidity of plums, cherries, peaches and apricots is calculated as malic acid and that of grapes as tartaric acid.

$$\% \text{ total acid} = \text{Factor} \times \text{titer}$$

Where original weight of sample was 25 gm. and dilution was 5

$$\text{Factor} = \frac{1}{10} \times \frac{\text{equiv. wt. of acid} \times \text{normality of NaOH}}{5 (\text{wt. of sample used})}$$

Equivalent wt. of acids:

Citric (mono-hydrate) = 70.0 gm.

Malic = 67.0 gm.

Tartaric = 75.0 gm.

Jams, Jellies and Marmalades

SULFUR DIOXIDE

Official Method

Principle

The sample is acidified and the evolved sulfur dioxide is swept with carbon dioxide or nitrogen into cold hydrogen peroxide where the sulfurous acid is oxidized to sulfuric acid. The latter is determined by titration with standard sodium hydroxide.

Reagents

1. Hydrogen peroxide - 3% solution. Dilute 200 ml. 30% hydrogen peroxide to about 1400 ml. in a 2000 ml. graduate. Mix by pouring solution back and forth from a 2000 ml. beaker to the graduate. Take 100 ml. portion of diluted solution (100 ml. graduate) and titrate in a 250 ml. beaker on pH meter with 0.1N NaOH to pH 4.1. Do not return this portion to main solution. Calculate amount NaOH required to neutralize the main solution; add this amount, stir, check the pH and filter through No. 1 Whatman paper. Pipette 10 ml. of the filtered solution into a 100 ml. volumetric flask and make up to volume. Pipette 5 ml. of this diluted solution into 500 ml. flask, add about 400 ml. water and 10 ml. 6N H₂SO₄ and titrate with 0.1N potassium permanganate to first permanent pink color. If an exact 3% solution is required, calculate as follows:

$$1 \text{ ml. } 0.1\text{N KMnO}_4 = 0.0017 \text{ gm. H}_2\text{O}_2$$

If A ml. of B N KMnO₄ are required

$$A \text{ ml. } B \text{ N KMnO}_4 = \frac{AB}{0.1} \times 0.0017 = 0.017 AB \text{ gm. H}_2\text{O}_2$$

$$\% \text{ H}_2\text{O}_2 = \frac{100}{5} \times \frac{100}{10} \times 0.017 AB = 3.4 AB\%$$

Adjust solution to 3% and store in a refrigerator.

2. Bromophenol blue - 0.05% solution. Dissolve 0.1 gm. in 2 ml.

0.1N sodium hydroxide and dilute to 25 ml. with water.

3. Sodium carbonate - saturated solution. Dissolve sufficient sodium carbonate (technical grade) to prepare a saturated solution.

Add several drops of phenolphthalein. Discard this solution when it becomes decolorized by adsorption of acids in the carbon dioxide.

Apparatus

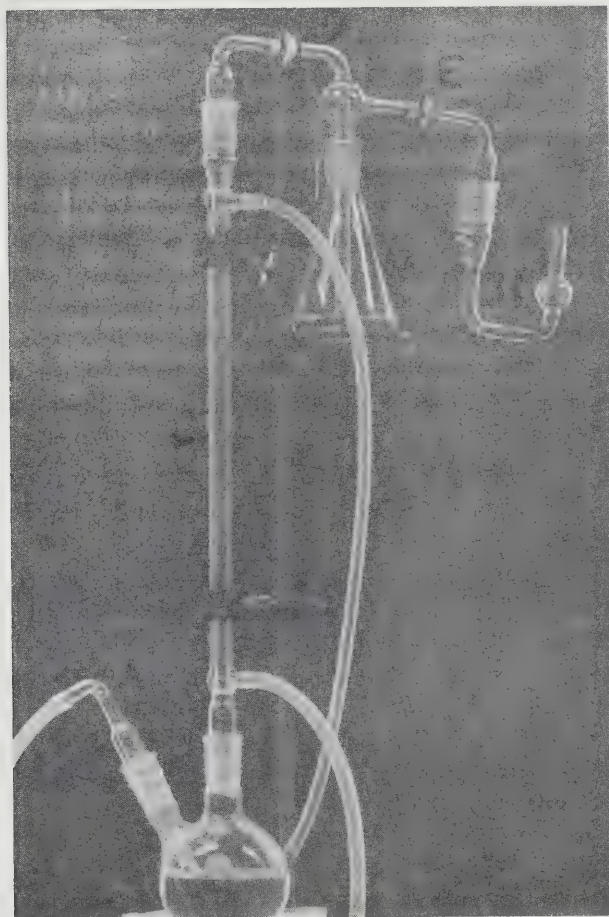
The apparatus illustrated in Figure 1 was obtained from a laboratory glassware manufacturer according to specifications submitted. The material is Pyrex throughout. All parts have either 24/40 standard taper or 18/9 spherical joints. Major dimensions are shown in footnotes to the illustration.

Procedure

Circulate cold water through condensers. Add 15 ml. of 3% hydrogen peroxide to the Erlenmeyer flask and 5 ml. to the trap. Assemble and connect to condenser. Weigh 50 gm. of blended sample and rinse into 500 ml. flask using 300 ml. water. Connect flask to condenser immediately, making sure all connections are well greased. Remove the gas inlet tube, and slowly add 20 ml. conc. HCl. Replace the tube and observe if bubbles enter the receiving flasks. If not, check joints for leaks. Adjust CO₂ (passed through a gas washing bottle filled with sodium carbonate solution) or nitrogen (99.9% pure) to give a flow of 6 to 12 bubbles per minute through the tube. Connect the 500-watt heaters and turn to the full position. In about 5 minutes, when solution starts to boil, adjust heaters to give

FIGURE I

All Glass Apparatus
For Sulfur Dioxide Determination ¹.



- A. Gas inlet tube
- B. 500 ml. round-bottom flask
- C. Condenser 400 mm. jacket length
- D-E. 18/9 spherical joints
- F. Special adapter
- G. 250 ml. Erlenmeyer flask
- H. Trap

1. The apparatus shown in Fig. 1 was designed by J. A. Kitson
of this laboratory.

a slow boil. Dried fruits or vegetables require one hour boiling. Thirty minutes is sufficient for all other products. Wash the hydrogen peroxide solution from the trap into the Erlenmeyer flask. Rinse the trap with water. Add 3 drops of bromophenol blue indicator and titrate with 0.1N NaOH solution to pale sky-blue end-point, using a 5 ml. microburette. (For samples very high in SO₂, use 50 ml. burette.) Run a blank titration on 20 ml. of hydrogen peroxide and correct results accordingly.

Calculations

$$1 \text{ ml. } 0.1\text{N NaOH} = 3.2 \text{ mg. SO}_2$$

$$\text{Factor} \times \text{titer} = \text{p.p.m. SO}_2$$

$$\text{Factor} = \frac{32 \times 1000 \times \text{normality of NaOH}}{\text{wt. of sample}}$$

References

- Association of Official Agricultural Chemists. Official Methods of Analysis, 8th Ed. pp. 507-509. Washington, D. C. 1955.
- Shipton, J. Estimation of sulfur dioxide in dried foods. Food Preservation Quarterly 14, 3: 54-56. 1954.

SOLUBLE SOLIDS

Principle

Soluble solids are determined with a refractometer equipped with a per cent sugar scale.

Procedure

Take representative portions of a well-mixed sample of jam or jelly free from seed and fibre, place on refractometer prisms and read directly at 20°. If temperature correction is necessary, use the correction factor given in Table I. It is preferable to have the instrument maintained at constant temperature by circulating water through the prisms. For very accurate results a correction should be made for water-insoluble solids as follows:

$$\% \text{ soluble solids} = \% \text{ solids by refractometer} \times \frac{(100-a)}{100},$$

where a = % water-insoluble solids.

pH

Principle

The effective acidity is determined by taking a direct reading on a pH meter.

Procedure

Standardize the pH meter with a pH 4.0 buffer solution.

Place 50 to 75 gm. of well-mixed sample in a 100 ml. beaker and read on pH meter. When first reading is completed, wipe electrodes with small piece of cotton soaked in distilled water. Rinse electrodes with water from wash bottle, dry with piece of filter paper and continue with the next determination.

TABLE I[#]

Temperature Corrections for the Standard Model of
Sugar Refractometer Calibrated for 20°C.

Temperature	Percentage of dry substance													
	5	10	15	20	25	30	35	40	45	50	55	60	65	70
	Subtract from dry-substance percentages													
15°C.	.29	.31	.33	.34	.34	.35	.36	.37	.37	.38	.39	.39	.40	.40
16	.24	.25	.26	.27	.28	.28	.29	.30	.30	.30	.31	.31	.32	.32
17	.18	.19	.20	.21	.21	.21	.22	.22	.23	.23	.23	.23	.24	.24
18	.13	.13	.14	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16	.16
19	.06	.06	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08
Add to dry-substance percentages														
21	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08	.08	.08
22	.13	.14	.14	.15	.15	.15	.15	.15	.16	.16	.16	.16	.16	.16
23	.20	.21	.22	.22	.23	.23	.23	.23	.24	.24	.24	.24	.24	.24
24	.27	.28	.29	.30	.30	.31	.31	.31	.31	.31	.32	.32	.32	.32
25	.35	.36	.37	.38	.38	.39	.40	.40	.40	.40	.40	.40	.40	.40
26	.42	.43	.44	.45	.46	.47	.48	.48	.48	.48	.48	.48	.48	.48
27	.50	.52	.53	.54	.55	.55	.56	.56	.56	.56	.56	.56	.56	.56
28	.57	.60	.61	.62	.63	.63	.64	.64	.64	.64	.64	.64	.64	.64
29	.66	.68	.69	.71	.72	.72	.73	.73	.73	.73	.73	.73	.73	.73
30	.74	.77	.78	.79	.80	.80	.81	.81	.81	.81	.81	.81	.81	.81

Proceedings of the Ninth Session of the International Commission for Uniform
Methods of Sugar Analysis, London, 1936.

Jams, Jellies and Marmalades

ARTIFICIAL FOOD DYES

Water-Soluble Coal Tar Dyes

Principle

The dye is absorbed on a piece of white woolen cloth from an acidified solution. Individual pieces of the cloth are moistened separately with ^{conc.} HCl, conc. H_2SO_4 , conc. NH_4OH and 10% NaOH. The colors developed are compared with those of known dyes.

This procedure is no longer recognized as official by the Association of Official Agricultural Chemists. However, it is still considered a useful and quick estimation of the presence of some artificial food dyes, particularly where the dye is present in pure form.

Procedure

Dilute 20 to 200 gm. sample with 1 to 3 volumes of water, add 3 or 4 drops of conc. HCl and a small piece of white woolen cloth (nun's veiling). Heat to boiling and then cool. Rinse the dyed cloth thoroughly in running water, squeeze out excess water and cut into four small pieces; place each in a separate depression of a white porcelain spot plate. Moisten separate pieces with conc. HCl, conc. H_2SO_4 , 10% NaOH and conc. NH_4OH .

The hue of many coloring matters varies markedly upon treatment with acids or alkalies. This variation is also influenced by concentration of reagents and quantity of dye present. An unknown dye color should be compared with that of a known dye at approximately the same visual density. Table II shows color changes produced on wool dyed with 0.1 to 0.5% solutions of permitted food dyes.

TABLE II

Color Reactions Produced on Dyed Fibers by Various Reagents

Coloring Matter	Hydrochloric Acid	Sulfuric Acid	10% NaOH Solution	Ammonium Hydroxide
Amaranth	Slightly darker	Violet to brownish	Dull brownish to orange-red	Little change
Erythrosine	Orange-yellow	Orange-yellow	No change	No change
Ponceau 3R	Little change	Little change	Dull orange	Little change
Ponceau SX	Deeper red	Deeper red	Orange-yellow	Orange-yellow
Tartrazine	Slightly darker	Slightly darker	Little change	Little change
Naphthol Yellow S	Almost decolorized	Very pale, dull brown	No change	No change
Light Green SF Yellowish	Pale orange-yellow	Yellowish brown	Decolorized	Decolorized
Brilliant Blue FCF	Yellow	Yellow	No change	No change

References

Association of Official Agricultural Chemists. Official Methods of Analysis, 7th Ed. p. 658, Washington, D. C. 1950.

PECTIN

As Calcium Pectate¹.

Principle

Pectin is precipitated as calcium pectate from an acid solution by the addition of calcium chloride. The calcium pectate precipitate is washed with water until chloride-free, dried and weighed.

Reagents

1. Acetic acid - normal solution. (approximate) Dilute 30 ml. C.P. Glacial acetic acid to 500 ml. with water.
2. Calcium chloride - normal solution. (approximate) Dissolve 55 gm. CaCl_2 (anhydrous) in water and dilute to 500 ml.
3. Silver nitrate - 1% solution. Dissolve 1 gm. AgNO_3 in water and dilute to 100 ml.

Procedure

Weigh 50 gm. of blended sample into an 800 ml. beaker. Add approximately 400 ml. of water and boil gently for one hour, replacing water lost by evaporation. Transfer contents of beaker to 500 ml. volumetric flask and make up to volume at 20°. Shake well and filter through No. 4 Whatman filter paper into 500 ml. Erlenmeyer flask.

After mixing the sample by rotating the Erlenmeyer flask, pipette duplicate 100 ml. aliquots of solution into an 800 ml. beaker. Add 300 ml. water and 10 ml. N NaOH from a pipette, stirring constantly, and let stand overnight.

Add 50 ml. of 1N acetic acid with stirring and allow to stand for 5 minutes. Add 25 ml. of 1N CaCl_2 solution with stirring. Allow

1. Modification of Carre and Haynes method by Dr. McInney, Food and Drugs Laboratory, Ottawa. 1944.

to stand for 1 hour. Heat to boiling and boil for one minute. Filter through 41H Whatman paper and wash with almost boiling water until chloride-free. (Test with AgNO_3 .) Transfer residue on filter paper to previously dried and weighed aluminum dishes. Evaporate to dryness on water bath and dry overnight in oven at 100° . Cool in a desiccator and weigh. Report as per cent calcium pectate.

Calculations

$$\frac{\text{wt. of calcium pectate} \times 100}{\text{wt. of sample}} = \% \text{ Ca pectate}$$

$$\frac{\text{wt. of calcium pectate} \times 100}{10} = \% \text{ Ca pectate}$$

References

Carré, M.H. and D. Haynes. The estimation of pectin as calcium pectate and the application of this method to the determination of the soluble pectin in apples. *Biochem. J.*, 16:60-69. 1922.

Jams, Jellies and Marmalades

TOTAL AND REDUCING SUGARS

Lane and Eynon Method

Principle

Invert sugar reduces the copper in Fehling's solution to red, insoluble cuprous oxide. The volume of the unknown sugar solution required to completely reduce a measured volume of Fehling's solution is determined by titration, using methylene blue as indicator.

Reagents

1. Fehling's solution. Prepare by mixing equal volumes of reagents 2 and 3 immediately before use.
2. Copper sulfate solution. Dissolve 69.28 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, dilute to 1000 ml. and filter through No. 4 Whatman paper.
3. Alkaline tartrate solution. Dissolve 346 gm. Rochelle salt (potassium sodium tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and 100 gm. NaOH in water and make up to 1000 ml.

Keep these solutions in separate containers until ready to use.
4. Methylene blue indicator. Dissolve 1 gm. methylene blue in 100 ml. of water.
5. Neutral lead acetate - 45% solution. Dissolve 225 gm. neutral lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, in water and dilute to 500 ml.
6. Potassium oxalate - 22% solution. Dissolve 110 gm. potassium oxalate in water and dilute to 500 ml.

An excess of lead acetate or potassium oxalate in the sugar solution will result in an error in the titration. Determine the amount of potassium oxalate solution necessary to precipitate the Pb^{++} from

2 ml. of the lead acetate solution as follows:

Into each of six 50 ml. beakers containing 25 ml. water, pipette 2 ml. aliquots of the lead acetate solution. To the beakers add 1.6, 1.7, 1.8, 1.9, 2.0 and 2.1 ml. potassium oxalate solution, respectively. Filter each through a 41H Whatman paper and collect the filtrates in 50 ml. Erlenmeyer flasks. To each of the filtrates add a few drops of potassium oxalate solution. The correct amount of potassium oxalate required is the smallest amount which, when added to 2 ml. of lead acetate solution, gives a negative test for lead in the filtrate, i.e., no precipitate forms.

The equivalent volumes should be marked on the bottles and employed when the solutions are used in sugar determinations.

Preparation of Standard Sugar Solution

Weigh 9.5000 gm. of pure sucrose on a watch glass. Transfer to a 400 ml. beaker, add 100 ml. of water and 5 ml. of conc. HCl. Let stand for a week at a temperature of 12-15° or 3 days at 20-25°. Transfer to a 1000 ml. flask and make up to volume at 20°. The 1 per cent solution thus obtained is stable for several months.

Neutralize the sugar solution for titration as follows:

Pipette 50 ml. of the standard invert solution into a 200 ml. volumetric flask. Using phenolphthalein as indicator add 20% NaOH until solution turns pink. Acidify with 20% HCl, adding it dropwise, until the pink color is dispersed. Repeat the procedure using 0.1N NaOH and 0.1N HCl. Make up to volume with water. Titrate against 10 ml. Fehling's solution as described below under "Standard Method of Titration". The equivalent volume of neutralized sugar solution is 20.37 ml. The titration should be within ± 0.05 ml., e.g., 20.32 to 20.42 ml.

Method of Titration

With solutions of unknown concentration, the incremental method is first employed and subsequent titrations are performed by the standard method. However, when the analyst is experienced, the single incremental titration will give results sufficiently accurate for practical control work.

Standard Method of Titration

Pipette 10 ml. of mixed Fehling's solution or 5 ml. each of Fehling's A and B solutions into a 250 ml. Erlenmeyer flask. Fill a 50 ml. burette, having a pinchcock instead of a glass stopcock, with the solution to be titrated. Run almost the whole volume required to reduce the Fehling's solution into the flask, so that not less than 0.5 ml. or more than 1.0 ml. is required later to complete the titration. Mix the contents of the flask. Heat to boiling on a 500-watt hot plate covered with a clean asbestos-filled wire gauze. Maintain the liquid in moderate ebullition for 2 minutes, then add 2 drops of the methylene blue solution, taking care not to allow it to touch the side of the flask. Complete the titration within 1 minute by adding 2 to 3 drops of sugar solution at 5 to 10-second intervals, until the indicator is completely decolorized. At the end-point the boiling liquid assumes the brick red color of precipitated cuprous oxide, which it had before the indicator was added.

The Incremental Method of Titration

Pipette 10 ml. of mixed Fehling's solution, or 5 ml. of each of A and B, into a 300 ml. flask as in the Standard Method. Add from the burette 15 ml. of the sugar solution or a larger volume if it is known to be insufficient to completely reduce the quantity of Fehling's solution

used. Mix and heat to boiling as in Standard Method. Boil for 15 seconds. If the color remains blue, indicating that the Fehling's solution is not completely reduced, make further 5 to 10 ml. additions of the sugar solution. Boil the solution for a few seconds after each addition until it is judged unsafe (i.e., only the faintest perceptible blue color remains) to add more sugar solution without risk of passing the end-point. Add 2 drops of methylene blue solution and complete the titration by adding the sugar solution dropwise until the indicator is completely decolorized. The accuracy of the Incremental Method is increased by approaching the end-point as rapidly as possible and keeping as nearly as possible to a total boiling period of 3 minutes.

Usually the total volume of sugar solution required by the Incremental Method is rather less than that required by the Standard Method. In practised hands the error resulting from this titration should not exceed 2 per cent and is rarely more than 1 per cent.

Procedure

Place 50 gm. of the jam in a 800 ml. beaker and add 400 ml. water. In order to prevent inversion of sugars during boiling extraction, neutralize the solution with 0.1N NaOH. (If acidity has been determined previously using a 5 gm. sample, then use same volume of 1N NaOH as was required of 0.1N NaOH to give a pH of 7.0 in the acidity determination.)

Boil gently for 1 hour with occasional stirring. Add boiling water to maintain the original level. Cool and transfer to a 500 ml. volumetric flask. Make up to volume and filter through No. 4 Whatman paper. Pipette a 100 ml. aliquot into a 500 ml. volumetric flask. Add slowly 2 ml. of neutral lead acetate solution. Let stand for 10 minutes, then

precipitate the excess of Pb^{++} with potassium oxalate as follows:
add the required amount of potassium oxalate solution as previously determined, shake well and filter through a 41H Whatman filter paper. Test the filtrate for unprecipitated Pb^{++} with a drop of potassium oxalate. If precipitate forms, add approximately 0.5 gm. crystalline potassium oxalate. Refilter and retest for Pb^{++} .

Reducing Sugars. Pipette 50 ml. of the clarified solution into 100 or 250 ml. volumetric flask. (The dilution depends on the concentration of reducing sugars present.) Make up to volume and titrate by the "Standard Method".

Total Sugars. Pipette 50 ml. of the clarified solution into 250 ml. Erlenmeyer flask. Add 5 gm. citric acid and 50 ml. water. Boil gently for 10 minutes to invert sucrose, then cool. Neutralize as outlined under "Preparation of Standard Sugar Solution". Transfer the solution to 250 ml. volumetric flask. Make up to volume and titrate by the "Standard Method".

Calculations

$$\text{Concentration of reducing sugar in mg. per 100 ml.} = \frac{\text{factor} \times 100}{\text{titer}}$$

$$\% \text{ reducing sugar} = \text{dilution} \times \frac{\text{factor}}{\text{titer}} \times \frac{100}{1000}$$

$$= \frac{\text{factor}}{\text{titer}} \times 10 \text{ (where dilution is 100)}$$

References

Atkinson, F. E. and C. C. Strachan. Candying of fruit in B.C. with special reference to cherries. Fruit Prod. J., 20: 132,166,199,229,262,310. 1941.

Table III - Factors for 10 ml. Fehling's Solution to be used

with Lane-Eynon Volumetric Method[#]

Titer in ml.	Invert sugar no sucrose	Titer in ml.	Invert sugar no sucrose
15	50.5	33	51.7
16	50.6	34	51.7
17	50.7	35	51.8
18	50.8	36	51.8
19	50.8	37	51.9
20	50.9	38	51.9
21	51.0	39	52.0
22	51.0	40	52.0
23	51.1	41	52.1
24	51.2	42	52.1
25	51.2	43	52.2
26	51.3	44	52.2
27	51.4	45	52.3
28	51.4	46	52.3
29	51.5	47	52.4
30	51.5	48	52.4
31	51.6	49	52.5
32	51.6	50	52.5

[#] Association of Official Agricultural Chemists. Official Methods of Analysis, 8th Ed. p. 906, Washington, D. C. 1955.

Jams, Jellies and Marmalades

ASH

Principle

The dried sample is ignited at 525° to a white ash.

Procedure

Weigh duplicate 5 to 10 gm. blended samples into 100 ml. flat-bottom platinum or porcelain dishes. Heat on water bath until water is expelled. Place slowly in muffle furnace at 525° and leave until white ash is obtained. Cool in desiccator and weigh. If black specks appear when water is added to the ash, the sample must be redried and placed in the furnace until a completely white ash is obtained. The time required varies with different products and must be determined by experiment.

TOTAL SOLIDS

Principle

A weighed portion of material is dried in a vacuum oven at a temperature not exceeding 70°. Drying time is determined by experiment and is considered sufficient when weighings made at 2-hour intervals do not differ by more than 3 mg.

Procedure

Weigh accurately in duplicate into large flat-bottom dishes 20 gm. of well mixed sample, or a quantity that will give not more than 3 to 4 gm. of dry material. If necessary, to secure a thin layer of the material, add a few ml. of water and mix thoroughly. Evaporate to dryness on a water bath and dry at 70° in a vacuum oven at 26 inches vacuum until consecutive weighings made at intervals of 2 hours do not vary more than 3 mg. Overnight drying is usually sufficient for most samples.

Calculations

$$\% \text{ total solids} = \frac{\text{dry wt.}}{\text{wt. of sample}} \times 100$$

FRUIT JUICES

ASCORBIC ACID

Indophenol Method

Principle

Aliquots in oxalic acid solution are titrated with standardized sodium 2:6-dichlorophenolindophenol dye to a faint pink color which persists from 5 to 10 seconds.

Reagents

1. Indophenol dye - 0.04% . Weigh 0.2 gm. sodium 2:6-dichlorophenol-indophenol. Dissolve in about 200 ml. hot water, filter through No. 4 Whatman paper into 500 ml. volumetric flask and make up to volume at 20°. Store in refrigerator.
2. Oxalic acid - 0.4%. Dissolve 4 gm. oxalic acid in water and dilute to 1000 ml.

Standardization of dye - Dissolve 2 to 3 gm. potassium iodide in approximately 5 ml. water in 50 ml. Erlenmeyer flask. Add 15 ml. dye with a pipette and then 10 ml. 1N HCl. Mix and let stand for two minutes. Titrate with freshly prepared 0.01N sodium thiosulfate (20 ml. 0.1N in 200 ml. volumetric flask at 20°) using 1 to 2 ml. starch until there is no change in color upon addition of one drop or fraction thereof. Complete the titration in one minute. Dye should be standardized every 48 hours and kept not more than two weeks. Store the dye solution in a refrigerator.

1 ml. dye equivalent to

$$\frac{1}{1000} \times \text{ml. Na}_2\text{S}_2\text{O}_3 \times N \text{ Na}_2\text{S}_2\text{O}_3 \times 88 \times 1000$$
$$\text{ml. dye}$$
$$= \text{mg. ascorbic acid.}$$

Procedure

Shake can well, determine vacuum and headspace. Pipette 50 ml. juice (25 ml. for apple juice) into 250 ml. volumetric flask, make up to volume with 0.4% oxalic acid and filter through No. 4 Whatman filter paper. Use a 5 or 10 ml. aliquot for titration, depending on amount of ascorbic acid present. Add approximately 15 ml. oxalic acid (0.4%) and titrate with 0.04% dye to a faint pink end-point lasting for 5 to 10 seconds. Titration must be completed within 1 minute and the total dye required should not exceed 1.0 ml.

Calculations

mg. ascorbic acid per 100 ml. juice = dye factor x titer

Using 25 ml. of juice made up to 250 ml. with oxalic acid
and a 5 ml. aliquot taken for titration

$$\frac{250}{5} \times \frac{100}{25} \times .2070 \times \text{titer} = 41.4 \times \text{titer}$$

= mg. ascorbic acid per 100 ml.

References

- Bessey, O. A. and C. G. King. The distribution of vitamin C in plant animal tissues and its determination. J. Biol. Chem. 103: 687-698. 1933.
- Strachan, C. C. Factors influencing ascorbic acid retention in apple juice. Canada Dept. Agr. Pub. 732. Tech. Bull. 40. 1942.

ASCORBIC ACID

Colorimetric Method

Principle

Ascorbic acid is extracted from the material in a Waring blender using oxalic acid. The decolorizing effect of the extracted ascorbic acid on indophenol dye is measured with a photoelectric colorimeter.

Apparatus

1. Photoelectric colorimeter. For a Klett-Summerson use filter No. 540.
2. Matched tubes. If matched tubes are not available mark 4 tubes as follows:

DW - distilled water

S - standard (also used later for unknown solution)

No. 1

No. 2

Use these tubes in the required sequence throughout the procedure.

Reagents

1. Stock ascorbic acid solution - 0.1%. Dry ascorbic acid crystals in dark over sulfuric acid. Dissolve 0.2 gm. in water and dilute to 200 ml.
2. Working standards (W.S.). Take 5, 10, 15, 20 and 25 ml. of stock ascorbic acid solution and make each up to 500 ml. Resulting solutions numbered 1 to 5 contain 1, 2, 3, 4 and 5 mg. ascorbic acid per 100 ml. respectively. Check each solution against standard iodine or 0.04% indophenol dye (i.e. use 20 ml. W.S. when using dye and 50 ml. W.S. with 0.01N iodine).
3. Dye - sodium 2:6-dichlorophenolindophenol. Dilute 30 ml. 0.04% dye to 1000 ml. (12.0 mg./liter) (0.0012%).

Standardization

To the four matched tubes add reagents as follows:

DW - 10 ml. distilled water

S - 1 ml. W.S. No. 1 + 9 ml. water. Mix

No. 1 - 1 ml. 0.4% oxalic acid

No. 2 - 1 ml. W.S. No. 1

Adjust galvanometer to zero with tube DW in instrument.

To tube No. 1 add 9 ml. dye, invert to mix, insert into instrument in place of DW and take galvanometer reading in 15 seconds. Record as L_1 .

Adjust galvanometer to zero with tube S in instrument. To tube No. 2 add 9 ml. dye, invert to mix, insert into instrument in place of tube S and take galvanometer reading in 15 seconds. Record as L_2 .

In succession, record L_1 and L_2 readings for each working standard, rinsing the tubes with distilled water and drying between each determination.

On graph paper, against concentration ascorbic acid in mg. per 100 ml. as abscissa, plot readings $L_1 - L_2$ for each working standard.

Draw standard curve.

Preparation of sample

Weigh 350 gm. 0.4% oxalic acid into blender jar. Add exactly 50 gm. of representative sample of solid material. Blend for 3 minutes and filter through No. 4 Whatman filter paper. If sample is juice, pipette 50 ml. into 250 ml. volumetric flask and make up to volume using 0.4% oxalic acid. This will be termed filtrate.

Procedure

Obtain reading L_1 as described under standardization.

To tube S add 1 ml. filtrate + 9 ml. water, mix and adjust galvanometer to zero.

To tube No. 2 add 1 ml. filtrate + 9 ml. dye, invert to mix, insert into instrument in place of tube S and take reading in 15 seconds. Record as L_2 .

From the standard curve find the concentration of ascorbic acid in mg. per 100 ml. filtrate corresponding to L_1 - L_2 .

Calculations

Dilution x ascorbic acid in mg. per 100 ml. filtrate = mg. per 100 gm. sample.

Note: Unknown must contain 0.01 to .05 mg. ascorbic acid per ml.

References

- Bessey, O. A. A method for the determination of small quantities of ascorbic acid and dehydroascorbic in turbid and colored solutions in the presence of other reducing substances. J. Biol. Chem. 126: 771-784. 1938.
- Evelyn, K. A., H. T. Mallory and C. Rosen. The determination of ascorbic acid in urine with the photoelectric colorimeter. J. Biol. Chem. 126: 645-654. 1938.
- Loeffler, H. J. and J. D. Ponting. Ascorbic acid. Rapid determination in fresh, frozen or dehydrated fruits and vegetables. Ind. Eng. Chem., Anal. Ed. 14: 846-849. 1942.

Fruit Juices

TOTAL ACIDITY

Principle

The total acidity is determined by titrating a diluted sample of juice with standard NaOH to pH 8.1 using a pH meter.

Procedure

Pipette 10 ml. of juice into 250 ml. beaker. Add 100 ml. water and titrate with 0.1N NaOH to pH 8.1 using a pH meter.

Calculation

Calculate per cent total acidity as the predominant acid present as outlined under acidity of Jams, Jellies and Marmalades.

SPECIFIC GRAVITY

Principle

Specific gravity is determined on a sample of juice using a hydrometer at the temperature specified.

Procedure

Cool about 200 ml. juice in 250 Erlenmeyer flask to temperature specified for the hydrometer. Rinse hydrometer graduate with about 50 ml. of cooled juice. Fill graduate with juice, insert the hydrometer and take reading. Read the hydrometer at the liquid surface level, not at the top of meniscus. Make sure hydrometer is floating freely when read.

SOLUBLE SOLIDS

Principle

The soluble solids are determined with a refractometer equipped with a per cent sugar scale.

Fruit Juices

Procedure

Take soluble solids reading at 20° using a refractometer. In the case of apple juice, the per cent soluble solids multiplied by 4 should be approximately equal to the last two figures of the specific gravity reading.

Example: Soluble solids = 12.0%

Specific gravity should be close to $4 \times 12.0 = 1.0\textbf{48}$

pH

Principle

The pH as measured directly with a pH meter indicates the effective acidity of the juice.

Procedure

Standardize the pH meter with pH 4.0 buffer.

Pour juice in 50 ml. beaker and determine pH. This sample can be used for flavor, color, aroma and clarity evaluation.

CANDIED FRUIT AND PEEL

TOTAL AND REDUCING SUGARS

Lane and Eynon Method

Preparation of sample

Pass sample through a food chopper and mix thoroughly with a spoon. Place in an air-tight container and store until ready for analysis.

Procedure

Proceed as under "Standard Method of Titration" for Total and Reducing Sugars in Jams, Jellies and Marmalades or use the rapid method described in this section.

TOTAL ACIDITY

Preparation of sample

Use sample as prepared for Total and Reducing Sugars.

Procedure

Proceed as under Jams, Jellies and Marmalades.

SODIUM BENZOATE

Preparation of sample

Use sample as prepared for Total and Reducing Sugars.

Procedure

Proceed as under Pickles.

SULFUR DIOXIDE

Preparation of sample

Prepare sample as under Total and Reducing Sugars.

Procedure

Proceed as under Jams, Jellies and Marmalades.

ARTIFICIAL FOOD DYES

Procedure

Proceed as under Jams, Jellies and Marmalades.

SOLUBLE SOLIDS

Procedure

Before sample is passed through a food chopper, take a portion of the syrup and make a soluble solids reading with a refractometer. Temperature correction should be applied if the instrument is not at 20°.

TOTAL AND REDUCING SUGARS

Rapid Extraction Procedure

This procedure has been used successfully for analysis of candied fruits, jams, jellies and fresh fruit. It is recommended primarily for control work where quick results are desirable and the number of samples to be analysed is small. The Lane and Eynon method as outlined under Jams, Jellies and Marmalades is generally used in routine analysis.

Procedure

Transfer 50 gm. prepared sample to a one-quart Waring blender jar using 250 ml. ice cold distilled water. The jar should be cooled in refrigerator prior to use. Add about 60 to 70 gm. distilled water ice (2 small cubes) and 2 to 3 drops capryl alcohol. Blend contents of jar for 2.5 minutes with the lid held firmly in place. Add an additional 60 to 70 gm. of ice, wash down sides of jar with a few ml. water and blend for another 2.5 minutes. Transfer contents to a 500 ml. volumetric flask, shake to remove entrapped air and make up to volume at 20°. Rinse blender jar with small portions of the macerate from the volumetric flask and discard the rinsings. Pour remaining contents of the volumetric flask into the blender jar, add sufficient long fiber, acid washed, asbestos to fill a 100 ml. beaker and blend for 1 to 2 seconds. Filter the slurry through a 9 cm. coarse-porosity sintered-glass filter, using vacuum when necessary. Take suitable aliquots of the filtrate for reducing and total sugar determinations using the "Standard Method" titration as outlined under Jams, Jellies and Marmalades.

References

Kitson, J. A., C. C. Strachan, and R. F. Cain. Rapid sugar extraction procedure for analysis of candied fruits, jams and fresh fruits.

J. Agr. Food Chem. 3: 862-864. 1955.

DEHYDRATED FRUITS AND VEGETABLES

DEHYDRATED APPLES

MOISTURE

Preparation of sample

Pass sample through food chopper and mix thoroughly, completing operation as quickly as possible to avoid loss of moisture and sulfur dioxide. Replace sample in air-tight container and hold until ready for analysis.

Procedure

Spread about 10 gm. of prepared sample over the bottom of a weighed aluminum dish provided with a tightly fitted cover. Begin weighing with the cover off while adding the sample, until slightly over 10 gm. Close the dish and weigh accurately.

Dry for 6 hours at 70° and 26 inches vacuum. Remove the dish cover during this operation. During the drying, admit to oven a slow current of air (2 bubbles per second) dried by passing through sulfuric acid. Replace the cover, cool dish in desiccator and weigh.

Calculations

$$\frac{\text{loss in wt.}}{\text{wt. of sample}} \times 100 = \% \text{ moisture}$$

SULFUR DIOXIDE

Preparation of sample

Prepare sample by passing through a meat chopper. Place in air-tight container and store until ready for analysis.

Procedure

Using a 25 gm. sample proceed as outlined in section for Jams, Jellies and Marmalades.

DEHYDRATED POTATOES, CARROTS, ETC.

MOISTURE

Preparation of sample

Comminute sample in Waring blender for 1 to 2 minutes. Avoid overheating the sample. Pass through No. 60 mesh sieve and place in an air-tight container.

Procedure

Weigh duplicate 2 to 3 gm. samples into previously dried and weighed aluminum dishes. Place in a vacuum oven and dry under the same ^{as} conditions/outlined for dehydrated apples.

Calculations

See section on Dehydrated Apples.

MINCEMEAT
SODIUM BENZOATE

Principle

In a saturated sodium chloride solution containing an excess of Na^+ , benzoic acid is converted into water-soluble sodium benzoate. On acidifying the sodium benzoate solution with excess hydrochloric acid, water-insoluble benzoic acid is formed. The benzoic acid is extracted with chloroform. The chloroform is removed by evaporation and the residue containing benzoic acid is dissolved in alcohol and then titrated with standard sodium hydroxide.

Preparation of sample

Prepare sample by passing it through a food chopper. Place sample in air-tight container and keep for analysis.

Procedure

Weigh out 100 gm. sample and transfer to 500 ml. volumetric flask with saturated NaCl solution. Add 10 ml. NaOH (10%), shake, and check alkalinity with pH paper, adding more base if necessary. Add enough salt to saturate the water in the sample, about 5 to 10 gm. per 100 gm. sample, depending on the product. Make up to volume with saturated salt solution, allow to stand 2 hours with frequent shaking, or overnight with occasional shaking.

Filter the extract through No. 4 filter paper into 500 ml. Erlenmeyer. Pipette 100 ml. filtered extract into 500 ml. separatory funnel and neutralize with HCl (1 + 3). (If 10 ml. NaOH was used previously, the maximum amount of acid required here is about 2 ml.) Add 5 ml. excess HCl (1 + 3).

Extract the aqueous aliquot with successive portions of chloroform, 35, 25, 20, 15 ml. Shaking must be gentle, though thorough, because an emulsion forms very rapidly, especially with glacé cherries and peel. With these products it is advisable to filter the chloroform extract through chloroform washed absorbent cotton into 6" evaporating dishes. With products such as pickles it may be possible to draw off the chloroform directly into the evaporating dish. If any emulsion is drawn off with the separated extract, the chloroform must be washed with water (two 15-ml. portions), since the aqueous layer may contain non-volatile acids such as citric acid which interfere with the subsequent titration. Evaporate the chloroform extracts to dryness with an air blast. As soon as the residue is dry, place the dish in a sulfuric acid desiccator and leave it overnight.

Dissolve the residue in 50 ml. alcohol (4 + 1). Stir the solution well, loosening any undissolved residue with a stirring rod, and decant into 250 ml. beaker. Rinse the dish with 50 ml. water, pouring the rinsings into the beaker. Titrate on a pH meter to pH 8.1, using 0.05N sodium hydroxide from a 5-ml. micro-burette. A blank titration should be made on the solution of alcohol (4 + 1).

Calculations

1 ml. 0.05N NaOH = 0.0072 gm. anhydrous sodium benzoate

$$\text{p.p.m.} = \frac{\text{titer} \times N \times .0072 \times \text{dilution factor} \times 1,000,000}{.05 \times \text{sample weight}}$$

$$= \text{titer} \times N \times 7200 \text{ (where dilution is 5)}$$

PICKLES
SODIUM BENZOATE

Procedure

See section under MINCEMEAT

SODIUM CHLORIDE
Chromate Indicator Method

Principle

An aliquot taken from a neutralized solution containing sodium chloride is titrated with a standardized solution of silver nitrate using potassium chromate as an indicator.

Reagents

1. Silver nitrate 0.0855N. Dissolve 14.526 gm. reagent grade silver nitrate in water and dilute to 1000 ml. Standardize against a solution containing 0.500 gm. reagent grade sodium chloride (dried at 110° before weighing) per 100 ml. of water. One ml. of silver nitrate solution is then equal to 1 ml. of sodium chloride, thereby simplifying the calculations. If a normality other than 0.0855 is used, calculate as given in section under calculations.
2. Potassium chromate. Dissolve 5 gm. potassium chromate in water and dilute to 100 ml.

Procedure

Take either a 20 gm. or 20 ml. sample. Neutralize to pH 5 to 7 with dilute sodium hydroxide. If a pH meter is not available, add methyl orange and sufficient alkali to change indicator from orange to yellow. Transfer the solution to 200 ml. volumetric flask, make up to volume, mix and filter. Pipette 50 ml. aliquot of filtrate into 150 ml.

Erlenmeyer flask, add 1 ml. of potassium chromate solution and titrate with standard silver nitrate solution. The end-point is the first permanent red color.

Good lighting should be provided for the titration since the end-point is extremely difficult to detect with poor illumination. The analyst should satisfy himself that he is able to reproduce his results with a satisfactorily high degree of precision, since certain individuals are color blind in respect to the particular color changes involved.

Calculations

$$\% \text{ NaCl} = \frac{\text{ml. silver nitrate}}{10}$$

If the sample is taken by volume rather than by weight report as per cent w/v.

Where normality other than 0.0855 is used

$$\begin{aligned} \% \text{ NaCl} &= \frac{\text{ml. AgNO}_3 \times N \text{ AgNO}_3 \times \text{equiv. wt. of NaCl} \times 100}{1000 \times \text{wt. of sample}} \\ &= \frac{\text{ml. AgNO}_3 \times N \text{ AgNO}_3 \times 58.45 \times 100}{1000 \times 5 \text{ (where dilution is 4)}} \end{aligned}$$

References

National Canners Association. Laboratory Manual for the canning industry, Section 21, p. 13. National Canners Association, Washington, D. C. 1954.

WINES AND CIDER

ALCOHOL

By Distillation and Hydrometer

Principle

A measured volume of sample is distilled and the distillate diluted to a definite volume, usually the original volume. The alcohol content of the distillate is determined by means of a hydrometer.

Procedure

Pipette 100 ml. sample into the distillation flask and add 50 ml. water. Add about a half spoonful of tannin if foaming occurs. If an abnormal quantity of acetic acid is present, neutralize exactly with N NaOH. Connect the flask to the condenser and turn on water. Place a 100 ml. volumetric flask in position to collect the distillate. With low heat distill about 90 to 95 ml. into the volumetric flask. Remove the volumetric flask, cool to 20° and make up to volume with water.

Note the temperature on the stem of the hydrometer. Cool the distillate to exactly this temperature in an ice bath. Fill the hydrometer cylinder with distillate, check temperature and insert hydrometer. Read the per cent alcohol at the bottom of the meniscus, that is, at the general level of the liquid. If the amount of alcohol in the sample is too high to be read on the hydrometer, dilute the distillate to a known volume, cool to required temperature and take another reading. Multiply the result by the dilution factor to obtain the percentage of alcohol.

A specific gravity hydrometer may be used instead of one reading in per cent alcohol. Tables are available which give the correlation between specific gravity of alcohol-water mixtures and per cent alcohol by volume or weight.

TOTAL ACIDITY

Principle

Total acidity is determined by direct titration with 0.1N NaOH to pH 8.1 using a pH meter.

Procedure

Pipette 10 ml. sample into a 250 ml. beaker. Add 100 ml. water and bring quickly to boil to expel CO₂. Do not continue boiling because volatile acids may be lost. Cool the sample and titrate to pH 8.1 with 0.1N NaOH using a pH meter. Record volume of NaOH required and calculate the total acidity as per cent tartaric acid. One ml. of 0.1N NaOH equals 0.0075 gm. tartaric acid. Acidity of apple cider is expressed as malic acid and 1 ml. 0.1N NaOH equals 0.0067 gm. malic acid.

TANNIN AND COLORING MATTER

Principle

A de-alcoholized sample is titrated with standard potassium permanganate using indigo solution as an indicator. Since other permanganate reducing substances are present, a blank titration is made after decolorizing the sample with activated carbon.

Reagents

1. Standard potassium permanganate solution. Dilute 576 ml. of 0.1N potassium permanganate solution to 1 liter. 1 ml. = 0.002 gm. of tannic acid $C_{14}H_{10}O_9$.
2. Indigo solution. Dissolve 6 gm. of sodium indigotin disulfonate in 500 ml. of water by heating; cool, add 50 ml. of conc. H_2SO_4 , dilute to 1 liter and filter.
3. Purified boneblack. Boil 200 gm. of powdered boneblack with two successive portions of HCl (1 + 3). Filter through hard filter paper, wash with boiling water until chloride-free. Place in a flask and keep covered with water.

Procedure

Place 100 ml. wine or cider in 300 ml. evaporating dish and remove alcohol by evaporating on hot plate to about 15 to 20 ml. Transfer to 100 ml. volumetric flask using water to loosen adhering sediment. Cool and make up to volume.

Pipette 10 ml. of the de-alcoholized sample into a 2000 ml. evaporating dish. Add 1000 ml. water and exactly 20 ml. indigo solution. Add the standard $KMnO_4$ solution 1 ml. at a time until the blue color

changes to green, then add a few drops at a time until color becomes golden yellow. Designate number of ml. of KMnO_4 solution as "a".

Transfer remaining de-alcoholized sample from the volumetric flask to a 250 ml. Erlenmeyer flask. Add about 2 teaspoons prepared boneblack and after 5 minutes with occasional shaking, filter.

Pipette 10 ml. of decolorized sample into a 2000 ml. porcelain evaporating dish. Add 1000 ml. water and exactly 20 ml. indigo solution. Titrate with KMnO_4 as directed above. Designate ml. KMnO_4 as "b".

Calculation

$a - b = \text{ml. of the } \text{KMnO}_4 \text{ solution required for oxidation of}$
 $\text{tannin and coloring matter in 10 ml. wine.}$

$\text{gm. tannic acid per 100 ml.} = 0.002 \times \text{ml. } \text{KMnO}_4.$

References

Cruess, W. V., M. A. Joslyn and L. G. Saywell. Laboratory examination of wines and other fermented products, pp. 66-69. Avi Publishing Co. Inc., New York, N.Y. 1934.

Wines and Cider

TOTAL AND REDUCING SUGARS

Principle

See section under Jams, Jellies and Marmalades.

Preparation of sample

Pipette 200 ml. sample into porcelain dish, exactly neutralize with N NaOH, calculating the amount required from previous acidity determination, and evaporate to about 50 ml. Transfer to 200 ml. volumetric flask, add 2 ml. lead acetate solution (45%), dilute to mark with water and let stand for 10 minutes. Add the required amount of potassium oxalate solution (22%) as determined for Total and Reducing Sugars under Jams, Jellies and Marmalades. Filter through No. 4 Whatman paper. Test the filtrate for absence of lead.

Reagents

See Total and Reducing Sugars under Jams, Jellies and Marmalades.

Procedure

Using above prepared extract, proceed as under "Standard Method of Titration" for Total and Reducing Sugars in Jams, Jellies and Marmalades.

References

Cruess, W.V., M.A. Joslyn and L.G. Saywell. Laboratory examination of wines and other fermented products, pp. 52-58. Avi Publishing Co. Inc., New York, N.Y. 1934.

TOTAL VOLATILE ACIDITY

Principle

Volatile acids are steam-distilled from the sample using a Hortvet type distillation apparatus and titrated with standard sodium hydroxide. The acids are calculated as acetic acid.

Procedure

Place about 100 ml. of wine or cider in a bottle and shake well to expel carbon dioxide. Let stand for a few minutes to allow escape of air bubbles.

Boil about 200 ml. of water in the outer heating flask. Most flasks are provided with an outside vent tube. The water may be boiled in the outer flask with the vent tube open to remove the dissolved CO₂, as well as to replace with steam the air in the flask surrounding the inner tube which may contain CO₂. Apply heat gently and turn on cold water through condenser.

With a pipette introduce a 20 ml. sample into inner tube and connect at once to the condenser. Increase the heat and bring the water in flask to vigorous boiling with the pinch cock on side of the tube open. When the water is boiling vigorously close the pinch cock. Steam passes through the 20 ml. sample carrying the volatile acid into the condenser. Collect the condensate in a graduated cylinder. Continue distillation until 100 ml. is collected.

Transfer the 100 ml. of distillate to 250 ml. beaker. Add about 50 to 100 ml. of water and titrate with 0.1N NaOH to pH 8.1.

Calculation

1 ml. 0.1N NaOH = 0.006 gm. acetic acid.

Note:

To determine whether all the volatile acids have been extracted, 50 ml. of distillate is first collected in one graduate and titrated, an additional 10 ml. portion is collected in a second graduate and added to the distillate in the first flask and titrated. Further 10 ml. portions are distilled over until an additional 10 ml. portion does not change the titration by more than one or two drops. Generally only 80 ml. of distillate is required.

References

- Cruess, W.V., M.A. Joslyn and L.G. Saywell. Laboratory examination of wines and other fermented products, pp. 33-44. Avi Publishing Co. Inc., New York, N.Y. 1934.
- Hortvet, J. The determination of total, fixed and volatile acids in wine. Ind. Eng. Chem. 1:31. 1909.

VOLATILE ACIDITY

Exclusive of SO_2

Principle

Following removal of the free sulfur dioxide by addition of barium hydroxide, the volatile acids are steam-distilled from the sample and titrated with standard sodium hydroxide.

Procedure

Pipette 50 ml. sample into 250 ml. beaker, add sufficient clear saturated $\text{Ba}(\text{OH})_2$ solution to bring mixture to pH 8.1. Allow to stand 30 minutes and maintain at pH 8.1 by addition of more $\text{Ba}(\text{OH})_2$ if necessary. Transfer to 100 ml. volumetric flask, dilute to volume and filter immediately through No. 2 Whatman paper. Pipette 20 ml. of filtrate into inner tube of volatile acidity distillation flask and add 1 ml. of H_2SO_4 (1 + 3). Place 150 ml. recently boiled hot water in outer flask and distill 100 ml. Using pH meter titrate with 0.1N NaOH to pH 8.1.

1 ml. 0.1N NaOH = 0.006 gm. acetic acid.

References

Association of Official Agricultural Chemists. Official Methods of Analysis, 8th Ed. p. 189. Washington, D.C. 1955.

Wines and Cider

EXTRACT

Hydrometer Method

The "extract" of wine and cider represents the alcohol-free soluble solids present and consists mainly of tartaric acid, potassium bitartrate, malic acid, protein, coloring matter, sugar and gums.

One method of determining the extract is to de-alcoholize the sample by boiling, dilute to the original volume and determine specific gravity with a Brix or Balling hydrometer. The other method is to evaporate a measured volume of sample to dryness and weigh the extract.

Procedure

Pipette 100 ml. sample into 400 ml. beaker. Add 50 ml. water and evaporate slowly to a volume of about 50 ml. Avoid loss by spattering. Transfer to 100 ml. volumetric flask and rinse the beaker with water. Add the washings to the flask. Cool and dilute to mark. Transfer to a cylinder and insert a Brix or Balling hydrometer. The reading will give the grams of extract per 100 ml. original sample. (For approximate purposes the refractometer reading gives a satisfactory result).

Oven Method.

Procedure

Place empty evaporating dishes into oven at 100° for 1 hour. Transfer to desiccator, cool and weigh. Pipette 50 ml. sample into evaporating dish and heat on water bath until the liquid has evaporated to a viscous consistency. Place dishes into vacuum oven at 70° and 26 to 28 inches vacuum for 8 hours. Place in desiccator, cool and weigh.

Calculations

$$\% \text{ extract} = \frac{\text{wt. of extract}}{\text{wt. of sample}} \times 100$$

SAUERKRAUT
TOTAL ACIDITY

Procedure

From the liquid portion of the product weigh 5 gm. into 250 ml. beaker. Add 100 ml. water, boil for a few minutes to drive off CO₂, cool and titrate with pH meter to pH 8.1 using 0.1N NaOH.

Calculations

$$\begin{aligned}\% \text{ Lactic acid} &= \frac{\text{titer} \times N \times \text{eq. wt.} \times 100}{1000 \times \text{wt. of sample}} \\ &= \frac{\text{titer} \times N \times 90.08 \times 100}{1000 \times \text{wt. sample}} \\ &= \frac{\text{titer} \times N \times 9.008}{\text{wt. of sample}}\end{aligned}$$

pH

Procedure

Adjust pH meter with pH 4.0 buffer solution.

Pour 50 to 75 ml. of juice into 100 ml. beaker and take pH reading.

FRUIT PRESERVED IN SULFUR DIOXIDE

SULFUR DIOXIDE

Official Method

Preparation of sample

Place portion of sample free from pits into Waring blender jar. Blend just long enough to mix into a slurry. Place sample back into air-tight container until ready for analysis.

Procedure

Using 25 gm. blended sample proceed as under section for Jams, Jellies and Marmalades.

Control Method

Principle

The sulfur dioxide solution is titrated directly against 0.05N iodine solution using starch as indicator. This control method is useful for determining the amount of sulfur dioxide in stock solutions or for estimating the sulfur dioxide content of fruit pulp preserved in this manner.

Reagents

1. Iodine solution - 0.05N. Dissolve 6.346 gm. iodine in a solution of 12 gm. potassium iodide in 100 ml. water and dilute to 1 liter.
2. Starch solution. Mix 0.5 gm. soluble starch with a little cold water (approx. 15 ml.), pour into 100 ml. hot water and boil 1 to 2 minutes. This solution is satisfactory for three to five days.

Procedure

With a 100 ml. pipette (inverted) remove approximately 100 ml. solution through the bung-hole of the barrel. If the solution is not clear,

filter through several layers of cheesecloth into a 400 ml. beaker.

Transfer the filtered solution to a 50 ml. burette as quickly as possible.

Pipette 10 ml. 0.05N iodine solution into a 500 ml. Erlenmeyer flask containing approximately 100 ml. water. Add 1 ml. starch solution. Titrate the SO₂ solution from the burette into the flask containing the iodine solution, rotating the flask frequently to keep the solution well mixed. When the color of the iodine solution becomes purple add the solution from the burette dropwise, stopping at the point where one drop dispells all color from the iodine solution.

Calculations

1 ml. 0.05N iodine reacts with 0.0016 gm. SO₂

$$\% \text{ SO}_2 = \frac{\text{ml. iodine} \times \text{normality of iodine} \times 0.16}{\text{ml. SO}_2 \text{ solution required}}$$

$$\text{p.p.m. SO}_2 = \% \text{ SO}_2 \times 10,000$$

References

Atkinson, F. E., and C. C. Strachan. Preservation of fruits with sulfur dioxide in British Columbia. Fruit Prod. J. 21: 5-8; 43-45; 60; 72-74; 110-112; 141-144; 153. 1941.

Wiegand, E. H. Process for the manufacture of maraschino cherries.

Western Canner and Packer 29: 33-34. 1937.

MISCELLANEOUS PROCEDURES

CALCIUM

Official Method

Principle

Calcium is precipitated as calcium oxalate. The precipitate is dissolved in hot dilute sulfuric acid and titrated with standard potassium permanganate.

Ashing

Weigh duplicate 25 gm. samples into glazed porcelain dishes. Evaporate to dryness on water bath and ash at a low red heat (not to exceed 525°) until free of carbon particles.

Reagents

1. Methyl orange - 0.05%. Dissolve 0.05 gm. methyl orange in water and dilute to 100 ml.
2. Oxalic acid - 2.5%. Dissolve 12.5 gm. oxalic acid in water and dilute to 500 ml.
3. Sodium acetate - 20%. Dissolve 100 gm. sodium acetate in water and dilute to 500 ml.
4. Saturated ammonium oxalate solution. To 12.0 gm. $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ add 200 ml. of water.

Procedure

Dissolve the ash obtained above in 50 ml. of (1 + 4) HCl and heat a few minutes. Be sure residue is acid. Filter through 15 cm. diameter No. 2 Whatman paper and wash thoroughly. Collect the washings in a 200 ml. volumetric flask. Make up to volume at 20°. To this filtrate or an aliquot, add two drops of methyl orange (pH 3 to 4), and then ammonium hydroxide (1 + 4) drop by drop, until the solution is just alkaline.

Add dilute HCl (1 + 4) drop by drop until the solution is just acid.

(When solution is cold and acid to the indicator, all the calcium phosphate is in solution. A small amount of phosphate or iron may remain undissolved at this point, but will go into solution when 0.5N acid is added).

When the solution is just acid, add 10 ml. of 0.5N HCl and 10 ml. of 2.5% oxalic acid. Heat the solution to the boiling point. Add 10 ml. of 20% solution of sodium acetate with constant stirring. Boil gently for 10 minutes. Add a few drops of saturated ammonium oxalate solution to make sure that all the calcium is precipitated. Hold overnight at 32° to 40°F.

Filter through 7 to 11 cm. diameter No. 40 Whatman paper into a beaker. Wash the precipitate free of chlorides with cold water (100 - 160 ml.). Wash the precipitate into a 400 ml. beaker using hot water. Keep the filter paper to add later in the titration. Make up to about 200 ml., add 5 ml. conc. H_2SO_4 or 10 ml. of H_2SO_4 (1 + 1) and heat to 70 to 80°C. Titrate hot with 0.1N KMnO_4 almost to completion (slight pink color). Add the filter paper in strips and complete titration to the first permanent pink color.

Calculations

$$1 \text{ ml. } 0.1\text{N } \text{KMnO}_4 = .002 \text{ gm. Ca.}$$

References

Association of Official Agricultural Chemists. Official Methods of Analysis, 8th Ed. p. 378. Washington, D.C. 1955.

Snell, D.F. and C.T. Snell. Colorimetric methods of analysis. Vol. II, 3rd Ed. D. Van Nostrand Co. New York. 1949.

Miscellaneous Procedures

CALCIUM

Rapid Method for Determining Calcium in Apple-Firming Baths

Principle

Murexide indicator produces an orange red or salmon pink color in a buffered sample (pH 12.0) containing calcium. When calcium has been treated so that it is completely held in a complex with versenate, the color changes to a violet blue described by some as orchid purple.

Reagents

1. Standard calcium chloride solution. Exactly 1 gm. of calcium carbonate is dissolved in dilute HCl, boiled, and, after cooling, diluted to 1 liter. One ml. of this solution equals 1 mg. calcium carbonate or 0.4 mg. calcium.
2. Standard versenate solution. Dissolve 4 gm. disodium dihydrogen ethylenediamine tetraacetate in approximately 800 ml. of water. If the pH of this solution is not between 4.25 and 5.0, adjust by adding a little sodium hydroxide. In this pH range the versenate standard is very stable and may be kept satisfactorily for 8 months or longer. Adjust this solution against standard calcium chloride solution so that 1 ml. equals 1 mg. as CaCO_3 or 0.4 mg. as Ca.
3. Sodium hydroxide solution - 1N. This reagent is used to adjust the sample to approximately pH 12.
4. Calcium indicator. Combine 0.2 gm. of ammonium purpureate (murexide) with 100 gm. of sodium chloride. Mix well and grind the mixture to 40 to 50 mesh. Potassium sulfate may be used as diluent instead of the sodium chloride. This dye is unstable in most solutions but is stable in a dry mixture such as this.

Procedure

Adjust 100 ml. of the firming solution to 20° and filter through a rapid paper such as Whatman No. 4 or a glass wool plug. If organic matter or precipitated salts are not removed, a slow reaction and indefinite end-point will result.

Pipette 50 ml. of the clear sample (20°) into 250 ml. porcelain evaporating dish or beaker. Add 2 ml. of 1N NaOH to the aliquot and stir. (This quantity of NaOH, except in unusual cases, gives approximately pH 12). Add 0.2 gm. of calcium indicator and stir. A calibrated spoon can be used for adding this indicator. If calcium is present the sample will turn a salmon pink or orange red.

Add the titrating solution slowly from the burette with continued stirring. When near the end-point, the solution turns light purple. The end-point is the final change to a violet blue or orchid purple and has been reached if additional titrating solution produces no further color change.

Calculation

$$\text{p.p.m. calcium (Ca)} = \frac{\text{ml. titrating solution} \times 400}{\text{ml. of sample}}$$

or

$$\text{p.p.m. calcium as calcium carbonate (CaCO}_3\text{)} = \frac{\text{ml. titrating solution} \times 1000}{\text{ml. of sample}}$$

References

- Betz, S.D. and C.A. Noll. Total hardness determination by direct colorimetric titration. J. Am. Water Works Assoc., 42: 49-56. 1950.
- Strachan, C.C. Rapid method for determining calcium in apple-firming baths. Can. Food Ind. 22: 25-27. 1951.
- Strachan, C.C., and A.W. Moyls. Rapid versenate methods for determining calcium in solutions and fruit and vegetable tissue for quality control. Food Technol. 6: 333-336. 1952.

Miscellaneous Procedures

TANNIN AND COLORING MATTER

Principle

In a neutral solution, tannin and coloring matter react with permanganate and are measured by titration, using indigo solution as an indicator. A blank titration must be made following treatment of the extract with activated carbon. The carbon adsorbs permanganate-reducing substances other than tannin, the most common of which are fruit acids.

Reagents

1. Standard potassium permanganate solution. Dilute 576 ml. of 0.1N potassium permanganate solution to 1 liter. 1 ml. = 0.002 gm. of tannic acid $C_{14}H_{10}O_9$.

Note: 0.1N $KMnO_4$ sometimes gives sharper end-point.

2. Indigo solution. Dissolve 6 gm. of sodium indigotin disulfonate in 500 ml. of water by heating; cool, add 50 ml. of conc. H_2SO_4 , dilute to 1 liter and filter.
3. Purified boneblack. Boil 200 gm. of powdered boneblack with two successive portions of HCl (1 + 3). Filter through hard filter paper, wash with boiling water until chloride-free. Place in a flask and keep covered with water.

Procedure

Use 50 gm. of light colored products such as peach, apple and pear, and 20 gm. of deeper colored products.

Transfer the sample to 500 ml. beaker, add 300 ml. of water and boil gently one hour, replacing the water lost by evaporation. Cool, transfer to 500 ml. volumetric flask and dilute to mark. Mix thoroughly and filter through No. 4 Whatman paper.

Pipette 400 ml. of filtrate into 600 ml. beaker, add 0.3 gm. powdered CaCO_3 and heat to boiling. Cool, transfer to 500 ml. volumetric flask and make up to volume. Add 0.5 gm. filtercel, mix thoroughly, and filter through No. 4 Whatman paper, refiltering if necessary until brilliantly clear.

Pipette 200 ml. of filtrate into 2 liter porcelain dish, add about 800 ml. of water and exactly 20 ml. of the indigo solution. Add standard KMnO_4 solution 1 ml. at a time, stirring vigorously until the blue color changes to green, then add a few drops at a time until the color becomes a golden yellow. Designate the ml. of KMnO_4 used as "a".

To the remaining filtrate add 1 gm. carbon and shake intermittently for 30 minutes. Filter through No. 4 Whatman paper, refiltering if necessary until clear. Pipette 200 ml. of the filtrate into the porcelain dish and add 800 ml. water and exactly 20 ml. of the indigo solution. Titrate with standard KMnO_4 in the manner described above. Designate the ml. of KMnO_4 solution required as "b".

Calculations

$a - b = \text{ml. KMnO}_4 \text{ solution required for oxidation of tannin}$
 $\text{and coloring matter.}$

$\text{gm. tannic acid in aliquot} = 0.002 \times \text{ml. KMnO}_4.$

$\% \text{ tannic acid} = \text{dilution} \times 0.002 \times \text{ml. KMnO}_4.$

References

- Hartman, B.E. The polybasic acids of fruits and fruit products. Tannin and coloring matter. J. Assoc. Offic. Agr. Chemists 26: 452-462. 1943.
- Strachan, C.C., A.W. Moyls, F.E. Atkinson and J. E. Britton. Chemical composition and nutritive value of British Columbia tree fruits. Canada Dept. Agr. Pub. 862. 1951.

Miscellaneous Procedures

ENZYME TESTS FOR ADEQUACY OF BLANCHING IN FROZEN VEGETABLES

Principle

This method is based upon measurement of the rate of color development in a guaiacol-hydrogen peroxide substrate under the catalytic influence of the enzyme present in the tissue. The reaction is brought about through the formation of an active peroxidase-peroxide complex which oxidizes the colorless guaiacol directly to an orange-brown end product.

Reagents

1. Guaiacol solution - 1%. Dissolve 1 gm. or 0.9 ml. guaiacol in 50 ml. ethyl alcohol and add 50 ml. water. Keep in a brown bottle.
2. Hydrogen peroxide - 1%. Dilute 1 part 3% H_2O_2 (free from preservatives) with 2 parts water.

Note: Glass dropping bottles of 100 ml. capacity are ideal containers. The reagents should be protected from light and stored in a refrigerator.

Testing reagents. The effectiveness of the reagents is determined by carrying out tests on two small pieces of fresh vegetable, one of which is boiled for 10 minutes and cooled. The unheated material should give a positive test, the heated a negative test.

Preparation of sample

Select representative material from portions that are exposed to the least heating, i.e., the central portions of the thickest pieces taken from positions farthest removed from surfaces exposed to the scalding medium. Use a stainless steel cutting knife.

For spinach, chard or similar leafy material, select a number of leaves and take the inch midrib portion commencing at the base of the leafy portion.

For asparagus spears, cut off and discard 3/4 inch from the butt end, then split the spears lengthwise.

For broccoli and cauliflower, split the stalk and head lengthwise.

For peas or other seed vegetables, cut each seed in half.

For string beans, cut 1/4 to 1/2 inch cross sections from a number of beans and split these cross sections lengthwise.

Procedure

Place the prepared material on a white porcelain saucer or evaporating dish. Add enough guaiacol solution to wet all of the cut surfaces, then immediately add a similar amount of hydrogen peroxide solution. At the end of 3 minutes note whether a reddish brown color has developed. If none is observed the test for peroxidase is negative. Neglect any color which may develop after 3 minutes. The reactions, as read at the end of 3 minutes are graded as follows:

- Negative - no color
- Trace - reddish brown specks
- Faint - up to 25% of the material colored
- Heavy - material a solid reddish brown color

References

- Atkinson, F.E., C.C. Strachan and A.W. Moyls. B.C. Processor's Handbook. Fruit and Vegetable Processing Laboratory, Canada Department of Agriculture, Experimental Farm, Summerland, B.C. September, 1947.
- Joslyn, M.A. Report on peroxidase in frozen vegetables. J. Assoc. Offic. Agr. Chemists 36: 161-178. 1953.

CRUDE FAT OR ETHER EXTRACT

For Fruit and Vegetable Products

Principle

Fat-soluble material is extracted from an oven-dried sample using a Soxhlet extraction apparatus. The ether is evaporated and the remaining material weighed.

Procedure

Weigh 50 gm. of blended sample into a 250 ml. beaker. Add about 75 ml. water and approximately 5 gm. asbestos. Mix and filter through No. 4 Whatman filter paper. If globules of fat are present on water layer, decant liquid into a separatory funnel and extract with several small portions of ether. If no fat is observed, liquid layer may be discarded. Keep the ether extract and combine it with sample prior to drying.

Place residue and filter paper in a thin aluminum foil dish and dry at 100° until moisture is removed, usually overnight.

Remove from oven and when cool, cut the dish and contents into small pieces and transfer directly into Soxhlet extraction thimble. Extract in the Soxhlet apparatus with anhydrous ether for at least 16 hours. If a hard gummy mass forms, remove thimble after about 10 hours and grind the sample to a fine powder in a mortar with sand. Return to the thimble and extract 10 hours longer.

Remove thimble from the apparatus and distill off most of the ether by allowing it to collect in the Soxhlet tube and pouring it off when the tube is nearly full. When the ether has reached a small volume, pour it into a small tared beaker through a small funnel containing a plug of cotton. Rinse the flask and filter thoroughly, using several small portions of ether.

Evaporate the ether on a steam bath at low heat, preferably under a current of air. Dry at 100° for 1 hour, cool and weigh.

Calculations

$$\frac{\text{wt. of fat soluble material}}{\text{wt. of sample}} \times 100 = \% \text{ crude fat}$$

References

National Cannery Association. Laboratory manual for the canning industry.

Section 20, p. 32. National Cannery Association, Washington, D.C. 1954.

APPENDIX

STANDARD SOLUTIONS

ACIDS

Hydrochloric Acid - 0.1N (3.646 gm. per liter)

Use conc. HCl - 37.3%

$\frac{3.646 \times 100 \text{ gm.}}{37.3}$ of 37.3% HCl gives 1 liter of 0.1N solution

Sp. Gr. of conc. HCl = approx. 1.19

Therefore volume of conc. HCl required

$\frac{3.646 \times 100}{37.3 \times 1.19} = 8.6 \text{ ml. per liter for .1N solution}$

Standardize against:

Standard 0.1N NaOH (titrate to pH 8.1)

Succinic Acid - 0.1N $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ (5.9023 gm. per liter)

Dry 5 to 6 gm. pure succinic acid in open weighing bottle at 105° for about 10 hours; cool and store in desiccator. Weigh 2.9511 gm., transfer to 400 ml. beaker and dissolve in 150 to 200 ml. of water. Pour the solution into 500 ml. volumetric flask, rinsing out the beaker several times to insure complete transference of the acid. Dilute to exactly 500 ml. and mix thoroughly.

This prepares an exact 0.1N solution.

Sulfuric Acid - 0.1N solution (4.904 gm. per liter)

Pour 3 ml. of conc. H_2SO_4 carefully into about 3 to 4 volumes of water. Cool, mix thoroughly and dilute to 1 liter. Standardize by titration with standard NaOH or KOH to the phenolphthalein end-point or to pH 8.1 with a pH meter.

Oxalic Acid - normal (63.023 gm. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per liter)

Decinormal or less conc. solutions are unstable and should be prepared fresh when needed; more conc. solutions may deposit some of the acid when cooled to low temperatures but they are fairly stable at room temperature when protected from light.

BASES

Sodium Hydroxide - normal (40.005 gm. per liter)

Dissolve 42 gm. sodium hydroxide sticks or pellets, of assay value 95% or better, in water and dilute to 1 liter.

Standardization of Sodium Hydroxide

1. For procedures using pH 8.1 as the end-point: against weighed portions of succinic acid

Dry succinic acid crystals at 105° for 10 hours and cool in desiccator. Take suitable portions of succinic acid (approx. 0.1 gm. for 0.1N NaOH and 0.05 gm. for 0.05N NaOH) and weigh accurately on an analytical balance. Dissolve in about 150 ml. water in 250 ml. beakers. Titrate with NaOH solution to pH 8.1. Check results by running standardizations in duplicate.

Calculations

$$\frac{\text{wt. of sample} \times 1000}{\text{titer} \times 59.05 \text{ (equiv. wt. acid)}} = N \text{ NaOH}$$

2. For procedures using bromophenol blue as indicator: against standard H₂SO₄

Standardization of H₂SO₄ against Na₂CO₃

Heat Na₂CO₃ at 105° for 24 hours. Weigh out exactly 1.3250 gm. and make up to 250 ml. This makes exactly 0.1N Na₂CO₃ solution.

Place 5 ml. H₂SO₄ plus 15 ml. water plus four drops bromophenol blue in 250 ml. beaker. Titrate with Na₂CO₃ to blue end-point or pH 4.1.

Standardization of NaOH with H₂SO₄

Place 5 ml. standard 0.1N H₂SO₄ plus 15 ml. water plus four drops bromophenol blue indicator in 250 ml. beaker. Titrate with NaOH solution to color end-point or pH 4.1.

For .05N NaOH use 2 ml. H₂SO₄.

OXIDIZING AND REDUCING SOLUTIONS

Potassium Dichromate - 0.1N (4.9035 gm. per liter). Grind about 5 gm. potassium dichromate in a mortar, heat at 120 to 140° for 2 to 4 hours. Cool in a desiccator and weigh to the nearest milligram. Transfer to 1 liter volumetric flask, dilute to volume and mix thoroughly.

$$\text{Normality} = \frac{\text{wt. of potassium dichromate}}{49.035}$$

Potassium Permanganate - 0.1N (3.1606 gm. per liter). Dissolve 3.3 gm. of dry KMnO_4 in 1 liter of water. Allow the solution to stand at least 24 hours in a clean glass-stoppered bottle. Carefully siphon through a clean glass tube into clean beakers, discarding the first 25 ml. of solution and the last inch of the solution in the bottle. Pour the solution back into a clean bottle and standardize with sodium oxalate.

Standardization with sodium oxalate

Weigh out accurately several 0.25 to 0.30 gm. samples of sodium oxalate having an assay value of 99.95%, transfer each portion to a 600 ml. beaker, and dissolve in 250 ml. of dilute sulfuric acid (5:95). Stir until the oxalate has dissolved, then add rapidly from a burette about 95% of the amount of permanganate needed for complete oxidation of the sample. Allow the solution to stand until the permanganate is decolorized, then heat to 55 to 60° and complete titration at this temperature, stirring gently and allowing each drop to become decolorized before adding the next.

$$\text{Normality of } \text{KMnO}_4 = \frac{1000 \times \text{gm. Na oxalate}}{\text{ml. of } \text{KMnO}_4 \times 67.00}$$

Sodium Thiosulfate - 0.1N (24.8192 gm. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter). Weigh 25.0 gm. and dilute to 1 liter. After mixing thoroughly, the solution is allowed to stand two weeks and the clear liquid siphoned off. The solution is standardized indirectly with potassium dichromate.

Standardization with potassium dichromate

Dissolve about 2 gm. potassium iodide in 10 ml. of water, and add 25 ml. of standard 0.1N potassium dichromate, dilute to about 200 ml. and titrate the liberated iodine at once with standard thiosulfate solution (until blue color just disappears). Instead of standard potassium dichromate solution, weighed quantities of potassium dichromate may be used.

Dissolve about 2 gm. potassium iodide in 10 ml. of water and add 10 ml. of (1 + 1) hydrochloric acid. To this solution, add 0.12 to 0.14 gm. potassium dichromate, dilute to about 200 ml. and titrate the liberated iodine at once with the thiosulfate solution, using starch as indicator. At the conclusion of this titration the solution is green in color, due to the chromic chloride present. The color change at the end-point from blue to light green is easily observed if the solution is diluted to at least 200 ml.

Iodine - 0.1N (12.693 gm. per liter). Dissolve about 13.5 gm. pure re-sublimed iodine in a solution of 24 gm. potassium iodide in 200 ml. of H_2O and dilute to 1 liter. The solution is standardized by titrating a known volume of standard thiosulfate with a few drops of starch solution as indicator.

INDICATORS

Phenolphthalein - pH range 8.3 to 10. Dissolve 1 gm. in 100 ml.

neutral ethyl alcohol or a mixture of equal parts of alcohol and water. Use 1 drop per 100 ml. solution.

Methyl red - pH range 4.4 to 6.0. Dissolve 1 gm. in 100 ml. 95% ethyl alcohol. This indicator is easily reduced with loss of color, and readings must be made shortly after adding to the solution.

Methyl orange - pH range 2.9 to 4.0. Dissolve 0.5 gm. in 1000 ml. water.

Bromophenol blue - pH range 3.0 to 4.6. Dissolve 0.1 gm. in 2.0 ml.

0.1N sodium hydroxide and dilute to 25 ml. with water.

Starch solution - 0.5%. Dissolve 0.5 gm. soluble starch in approximately 15 ml. cold water and pour into 100 ml. hot water. Boil 1 to 2 minutes.

Cleaning solution

Sodium or potassium dichromate (commercial)	40 gm.
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Water	150 ml.
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Dissolve with a little heat if necessary, then cool to room temperature and add slowly 230 ml. conc. sulfuric acid (tech. grade).

Note: As a precaution this solution should always be prepared over a sink.

CAN MARKING INK

The chemical ink prepared by this procedure can be used to write code marks on tin cans and also to write on galvanized iron labels.

Procedure

Pour 50 ml. conc. hydrochloric acid into 50 ml. water in a pyrex beaker. (Gives about 6N HCl). Dissolve 10 gm. antimony trichloride and 5 gm. copper sulfate in the 6N hydrochloric acid solution and mix well. Store ink in a glass stoppered bottle. Avoid contact with the skin.

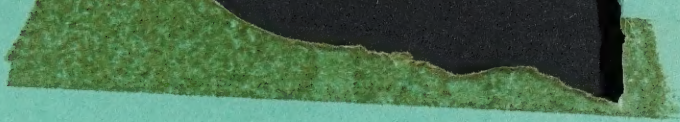
Note: Antimony trichloride must be stored at 32 to 34°F.

Applying the ink

This ink is very corrosive and should be applied with a glass pen. If such a pen is not available, a sharpened hardwood skewer can be used.

Commercial black ink

A commercially prepared black ink provided with the Flo-Master Marking Set, manufactured by Cushman and Denison Mfg. Co., New York 11, N.Y., has been used in this laboratory and found satisfactory for the range of temperatures encountered in processing work.



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